

I. POLYAZINES
II. CYCLIC POLYACETALS

BY

HAROLD WAYNE HILL, JR.

B.A., James Millikin University, 1947

M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS

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I. POLYAZINES

INTRODUCTION

The reaction of unsubstituted hydrazine salts and carbonyl compounds may proceed in either of two ways: (1) the hydrazine salt may react with one mole of the carbonyl compound to form a hydrazone, (2) the hydrazine may react with two moles of carbonyl compound to form an azine. In the case of ketones, the reaction usually stops at the hydrazone stage. However by the proper choice of reaction conditions, azine formation may be favored. On the other hand, aldehydes react with hydrazine so readily that it is very difficult, if not impossible, to stop the reaction at the hydrazone stage and azine formation occurs spontaneously. Thus it is evident that hydrazine may act as a bifunctional molecule in its reaction with carbonyl compounds.

Knowing that hydrazine can act as a bifunctional molecule, the question arises as to whether or not it would be possible to form a polymer by the reaction of a dicarbonyl compound and hydrazine. The preparation of polyazines by this method has received only a small amount of attention in the past. Although polyazines formed by the interaction of hydrazine salts and diketones have been studied to a limited extent (1), those obtained from dialdehydes and hydrazine represent a new class of organic polymers. Thus it has been of interest to determine the conditions necessary for the formation of these polyazines and to compare the ease of formation and properties of the polyazines obtained from aromatic dialdehydes and aliphatic dialdehydes.

DISCUSSION OF RESULTS

Polyazines have been prepared from the aromatic dialdehydes such as terephthalaldehyde and isophthalaldehyde. These polyazines are quite high-melting, insoluble in all solvents and have molecular weights in the range 500 to 1000. The great

insolubility seriously limits the molecular weight of the aromatic polyazines.

Polyazines cannot be formed from simple aliphatic dialdehydes such as malonaldehyde and succinaldehyde. Tar formation through aldol-type condensations predominates over polyazine formation. This is in accord with the observation that monoaldehydes in the aliphatic series give rather low yields of azines.

Substituted aliphatic dialdehydes which do not readily aldolize can be made to form polyazines by reaction with hydrazine sulfate. However the azine formation reaction does not produce high molecular weight polymers. Thus 2,4-dimethyl-2-methoxymethylglutaraldehyde gave a liquid polymer with molecular weight in the range 1500 to 2100.

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II. CYCLIC POLYACETALS

INTRODUCTION

The reaction between alcohols and carbonyl compounds, especially aldehydes, to form acetals is a well-known reaction. Acetals of high-boiling alcohols may also be formed from acetals of low-boiling alcohols by an exchange reaction in which the low-boiling alcohol is removed by distillation. Thus linear polyacetals have been prepared from dibutyl formal and high molecular weight glycols by the exchange technique (1). Linear polyacetals have also been prepared by the interaction of glycols and acetylene (2).

Both of the above polymerization methods involve an intermolecular combination. No work has been reported in which

the glycol unit and the aldehyde or acetal unit were in the same molecule. The purpose of this investigation was to synthesize a monomer which contained both a glycol unit and an acetal unit and to study the method of polymerization of this monomer. The monomer chosen for this study was 5-hydroxy-4-hydroxymethylvaleraldehyde diethyl acetal.

DISCUSSION OF RESULTS

The alkylation of malonic ester with β -chloropropionaldehyde diethyl acetal in the presence of sodium ethoxide and a small amount of sodium iodide produced 3,3-diethoxy-1-propylmalonic acid diethyl ester. Preliminary experiments on the action of lithium aluminum hydride on acetal indicated that the acetal linkage was unaffected. Thus the reduction of the alkylated malonic ester with lithium aluminum hydride produced 5-hydroxy-4-hydroxymethylvaleraldehyde diethyl acetal when the reaction mixture was worked up in basic media. Bulk polymerization of this monomer in the presence of a trace of ferric chloride gave a cyclic polyacetal which melts at 78-80°C. and had a molecular weight of approximately 400. The infrared spectrum of this polymer shows a strong absorption band in the region of the hydroxyl stretching vibration and no absorption in the region where an unconjugated aldehyde group would be expected. This indicates that polymerization proceeds through an initial hemiacetal formation and the polymer formed contains one oxygen atom in the ring and one oxygen atom in the linear portion between the rings, rather than both oxygen atoms in the cyclic portion.

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VITA

Harold Wayne Hill, Jr. was born on October 17, 1924, in Springfield, Illinois. After attending the public schools of Springfield and Decatur, Illinois, and graduating from Decatur High School in June, 1942, he entered James Millikin University, Decatur, Illinois. Following service in the Army of the United States from June, 1944, to April, 1946, he reentered James Millikin University and received the degree of Bachelor of Arts in June, 1947. From September, 1946, to August, 1947, he was an Assistant Instructor at James Millikin University. In September, 1947, he entered the Graduate College of the University of Illinois, where he received the degree of Master of Science in August, 1948. He held a Teaching Assistantship from February, 1948, to August, 1949, and the Allied Chemical and Dye Corporation Fellowship from September, 1949, to June, 1950.



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